# Reconstructions of the GaN(000$\bar{1}$) Surface

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Reconstructions of the GaN(000$\bar{1}$) surface are studied for the first time. Using scanning tunneling microscopy and reflection high-energy electron diffraction, four primary structures are observed: $1 \times 1$, $3 \times 3$, $6 \times 6$, and $c(6 \times 12)$. On the basis of first-principles calculations, the $1 \times 1$ structure is shown to consist of a Ga monolayer bonded to a N-terminated GaN bilayer. From a combination of experiment and theory, it is argued that the $3 \times 3$ structure is an adatom-on-adlayer structure with one additional Ga atom per $3 \times 3$ unit cell. [S0031-9007(97)04507-9]

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Gallium nitride and other III nitrides have attracted considerable interest recently because of their application for blue light-emitting diodes and lasers [1]. These materials have several unique properties compared to the more conventional III-V semiconductors (GaAs, InP, etc.): they exist in both cubic (zinc blende) and hexagonal (wurtzite) form, they are refractory, and some of the materials have large band gaps. The relatively small size of nitrogen, compared to Ga or In, in these compounds leads to a number of unique surface structures, which have begun to be explored both experimentally and theoretically for the (001) growth surface of cubic GaN [2,3]. However, for the technologically more relevant (0001) growth surface of hexagonal GaN, very little is known concerning its structure aside from several reports of $2 \times 2$ and other reconstructions based on reflection high-energy electron diffraction (RHEED) [4]. It is important to understand the surface structures of these materials, since this knowledge will impact our ability to achieve high quality epitaxial growth of the materials as required for optoelectronic applications.

In this Letter we report the first observations of reconstructions on the GaN(000$\bar{1}$) surface. The reconstructions are studied using scanning tunneling microscopy (STM), RHEED, and *ab initio* calculations. We find four dominant reconstructions, which in order of increasing surface Ga/N ratio are given by $1 \times 1$, $3 \times 3$, $6 \times 6$, and $c(6 \times 12)$. From among a number of candidate structures, the $1 \times 1$ reconstruction is found to consist of a monolayer (ML) of Ga atoms, located in atop sites above the N atoms of a N-terminated bilayer. This is a novel structure, with no known analog among other semiconductor surfaces. It is energetically feasible because of the much larger size of the Ga atoms compared to N atoms. For the $3 \times 3$ reconstruction, we find experimentally that it consists of a single additional Ga atom per $3 \times 3$ unit cell. Theoretically, the most plausible model for such a structure consists of the additional Ga atom in a threefold coordinated site just above the adlayer. Substantial in-

ward relaxation of the Ga adatoms is found, accompanied by large lateral relaxation of the Ga adlayer.

It is important to note that the (0001) and (000$\bar{1}$) surfaces of GaN are inequivalent (by convention, the [0001] direction is given by a vector pointing from a Ga atom to a nearest-neighbor N atom). Thin films having either surface polarity have been grown [5], although for growth by molecular beam epitaxy (MBE) the conditions which determine the surface polarity are not well understood [6]. The reconstructions studied in the present Letter are prepared on the (000$\bar{1}$) surface, with this assignment being made on the basis of (1) the observed reconstructions, which differ from those seen by both other workers [4] and ourselves [6] on surfaces believed to be (0001), (2) the theoretical studies presented here, which do not yield any acceptable models for a $1 \times 1$ structure on the (0001) face, and (3) convergent beam electron diffraction studies on our samples, which compared with theoretical simulations favor the assignment of (000$\bar{1}$) polarity [7].

The experiments are performed in an MBE system equipped with STM. Growth is performed on solvent-cleaned sapphire(0001) substrates, heated first to 1000 °C under a nitrogen plasma for 30 min. The substrate temperature is then reduced to 685 °C, and the growth is initiated. During the first few hundred angstroms of growth, the substrate temperature is gradually increased to about 775 °C. After growing a 2000 Å thick film, the growth is stopped and the sample is annealed at 800 °C for 15 min. The resulting film surface consists of atomically flat terraces up to a micron in width and exhibits a $1 \times 1$ structure. Depositing additional Ga atoms onto this surface results in the $3 \times 3$, $6 \times 6$, and $c(6 \times 12)$ reconstructions. Ga flux rates were calibrated using an *in situ* water-cooled crystal thickness monitor, at 20 °C.

STM images of our GaN surfaces are displayed in Fig. 1. Figure 1(a) displays a large-scale view of the surface, prepared in this case with Ga coverage intermediate between the $3 \times 3$ and $6 \times 6$ reconstructions. Coexisting with those structures we also occasionally observe small
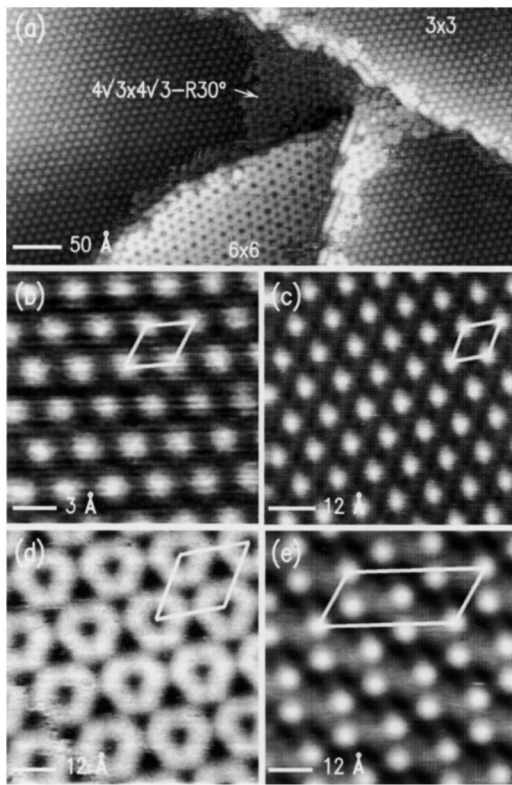
FIG. 1. STM images of the GaN(000$\bar{1}$) surface displaying (a) mixed reconstructions, with dislocation near center of image, (b) $1 \times 1$, (c) $3 \times 3$, (d) $6 \times 6$, and (e) $c(6 \times 12)$ reconstructions. Sample bias voltages are $+1.0$, $-0.75$, $-0.1$, $+1.5$, and $+1.0$ V, respectively. Tunnel currents are in the range $0.03-0.11$ nA. Gray scale ranges are 4.2, 0.17, 0.88, 1.33, and 1.11 Å, respectively. Unit cells are indicated with edges along $\langle 11\bar{2}0 \rangle$ directions.

areas of a somewhat disordered $(4\sqrt{3} \times 4\sqrt{3})$-$R30°$ structure, as indicated in the image. The atomic steps seen in Fig. 1(a) all have height of about 2.6 Å. A screw dislocation is seen emerging near the center of the image, with component of the Burgers vector in the [0001] direction of $c = 5.19$ Å. Such dislocations are commonly imaged on our surfaces. We point out that all the reconstructions observed in this study are stable only to temperatures up to $100-300$ °C, at which point a reversible phase transition occurs to a $1 \times 1$ structure as seen by RHEED. We associate this transition with an order-disorder transition of the Ga adatoms atop the $1 \times 1$ structure, evidence for which is seen even at room temperature by characteristic "glitchy" behavior in the images near certain domain boundaries indicative of adatom motion [8].

Detailed STM images for the $1 \times 1$, $3 \times 3$, $6 \times 6$, and $c(6 \times 12)$ reconstructions are shown in Figs. 1(b)–1(e), along with unit cells for each. The $1 \times 1$ appears as a hexagonal array of corrugation maxima, with a lateral spacing equal to the $c$-plane lattice constant of GaN, 3.19 Å. The $3 \times 3$ is similar in appearance but displays an asymmetry within the unit cell as well as additional

structure at lower biases. The asymmetry of the unit cell reflects the fact that each GaN bilayer has only threefold symmetry. STM images confirm that this asymmetry reverses upon descending a single bilayer-high step on the surface. The $6 \times 6$ is made up of ring-shaped structures. Each ring has threefold symmetry with lobes from three neighboring rings coming close together. This results in two different kinds of "holes" around the rings, one appearing deeper than the other. The $c(6 \times 12)$ reconstruction is qualitatively different in appearance from the previous three. Rowlike structures are observed running parallel to $\langle 1\bar{1}00 \rangle$ directions of the crystal. Circular corrugation maxima appear in pairs along the rows; there are two possible angular orientations of these pairs of maxima with respect to the row directions in addition to the three possible row directions. Voltage dependence of the STM images for each reconstruction has been studied; no strong dependence is observed, except for the $c(6 \times 12)$ structure where the appearance of the rowlike features differs between empty and filled states.

For determining structural models of the observed reconstructions, an important constraint is the number of Ga (and N) atoms involved in each structure. These quantities have been studied by observing the dependence of the surface reconstructions on the amount of Ga deposited. Initial experiments were performed at a sample temperature of 630 °C. Results are shown in Fig. 2(a), where we plot the fractional coverage of each major reconstruction, as determined by STM. Also shown are representative RHEED patterns for each of the reconstructions. While the amount of Ga deposited is known for Fig. 2(a) (Ga flux of 0.058 ML/s), the sticking coefficient at that sample temperature was found to be much less than unity so that an absolute determination of surface Ga coverage was not possible. Further experiments were performed with a sample temperature of 60 °C, as shown in Fig. 2(b). In this case, the RHEED intensities were used for determining the fractional coverage of a particular reconstruction. Focusing on the formation of the $3 \times 3$, we find from Fig. 2(b) that this structure is formed at a coverage of $0.145 \pm 0.025$ ML, corresponding to $1.3 \pm 0.2$ atoms per $3 \times 3$ unit cell. Since the number of atoms per unit cell must be an integer, we conclude that the $3 \times 3$ structure contains one additional atom per $3 \times 3$ cell compared with the $1 \times 1$. (The observed value is slightly greater than 1, probably because the sticking coefficient at 60 °C is slightly less than that for the thickness monitor used to calibrate the flux.)

Total energy calculations have been performed within the local density functional theory using first-principles pseudopotential methods similar to those employed in previous studies of GaN and AlN [3]. Reconstructions for both the (0001) and (000$\bar{1}$) polarities have been examined, and for each polarity the relative stabilities of possible structures have been determined within the thermodynamically allowed range of the Ga chemical
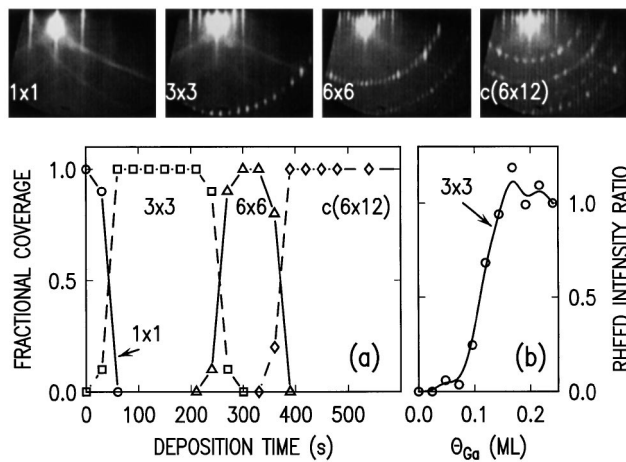
FIG. 2.    (a) Fractional coverage of $1 \times 1$, $3 \times 3$, $6 \times 6$, and $c(6 \times 12)$ reconstructions vs Ga deposition time, determined by STM imaging of the surfaces. Sample temperature during deposition was 630 °C. RHEED patterns corresponding to the different reconstructions are shown in the upper part of the figure. RHEED beam direction is along $[11\bar{2}0]$. (b) Ratio of RHEED intensities of the $(\frac{2}{3}\,0)$ and $(1\,0)$ streaks vs amount of Ga deposited in monolayers (1 ML = $1.14 \times 10^{15}$ atoms/cm$^2$). Sample temperature during deposition was 60 °C. All curves between data points are drawn as guides to the eye.
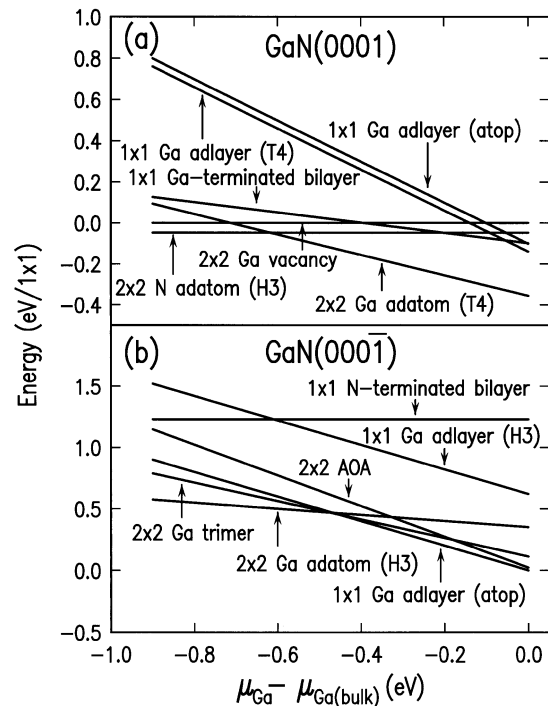


FIG. 3.    (a) The relative energies calculated for possible models of the GaN(0001) surface are shown as a function of the Ga chemical potential. (b) Relative energies for GaN($000\bar{1}$) surfaces. The zeros of energy in (a) and (b) are not related.

potential: $\mu_{\text{Ga(bulk)}} - \Delta H < \mu_{\text{Ga}} < \mu_{\text{Ga(bulk)}}$. Our calculations indicate that $\Delta H$, the heat of formation of GaN, is equal to 0.9 eV, in good agreement with the experimental value, 1.1 eV. The calculations have been performed with a plane wave cutoff of 60 Ry and with the Ga $3d$ states included in the valence band.

During the initial stages of the investigation we focused on the (0001) surface, but discovered that each of the $1 \times 1$ structures examined could be shown to be energetically unfavorable with respect to various structures having $2 \times 2$ periodicity. The relative formation energies calculated for the most relevant structures are shown in Fig. 3(a). Under N-rich conditions we find a $(2 \times 2)$-$H3$ N-adatom model to be most stable, and under Ga-rich conditions we find a $(2 \times 2)$-$T4$ Ga-adatom model is favored. Both the ideal topology $1 \times 1$ surface (consisting of a Ga-terminated bilayer) and the $1 \times 1$ Ga adlayer (comprised of a monolayer of Ga above the Ga-terminated bilayer) are energetically unfavorable. The $1 \times 1$ N adlayer is highly unstable. On the basis of these results we surmise that there is no stable $1 \times 1$ structure for the GaN(0001) surface. We emphasize, however, that the $2 \times 2$ Ga- and N-adatom models are each good candidates to explain the $2 \times 2$ structure observed in RHEED studies of the (0001) surface [4].

Not finding a stable $1 \times 1$ structure for the (0001) polarity, we turned our attention to the ($000\bar{1}$) surface. As shown in Fig. 3(b) we find the $1 \times 1$ Ga adlayer structure to be stable under Ga-rich conditions. Other structures, including the $(2 \times 2)$-$H3$ Ga adatom, are

predicted to be more stable under N-rich conditions, but there is a substantial range where the $1 \times 1$ Ga adlayer is the preferred structure. In the stable $1 \times 1$ model a full monolayer of Ga atoms sit directly atop the N atoms, with the Ga-N bond length equal to 1.99 Å. The Ga-Ga separation in the adlayer, 3.19 Å, is considerably larger than a typical Ga-Ga separation of 2.7 Å in bulk Ga. However, we find that the structure is stabilized by metallic bonding within the adlayer: a large overlap of the $p_x$ and $p_y$ orbitals of the Ga adlayer atoms gives rise to an energy dispersion of the surface states derived from these orbitals which is much greater than the bulk band gap. Consequently, the Fermi energy is located near the bottom of the band gap and there is no occupation of high energy Ga dangling bond states. We have also found that the $1 \times 1$ adlayer is stable with respect to adding Ga adatoms in threefold coordinated sites to create either a $2 \times 2$ adatom-on-adlayer (AOA) structure or a $\sqrt{3} \times \sqrt{3}$ AOA structure. On the basis of energetics, the GaN($000\bar{1}$)$1 \times 1$ Ga adlayer is the best candidate to explain the $1 \times 1$ structure observed here; this structure is illustrated in Fig. 4(a).

Calculations have also been performed for several possible models of the $3 \times 3$ surface. Because of the large size of the $3 \times 3$ unit cell these calculations were performed with the Ga $3d$ electrons treated as part of the core using the nonlinear core correction (nlcc) [9]. Structural models having one, two, or three additional
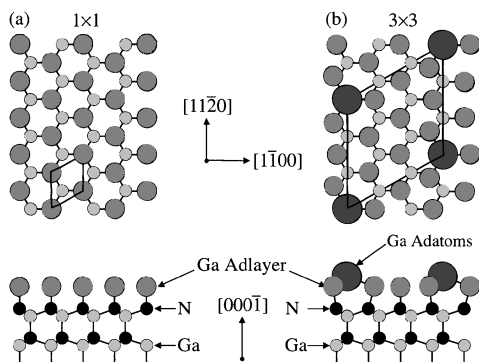
FIG. 4. Schematic view of structures determined for the (a) $1 \times 1$ Ga adlayer and (b) $3 \times 3$ adatom-on-adlayer reconstructions of GaN(000$\bar{1}$). For the $3 \times 3$ structure, the lateral (in-plane) displacement of the adlayer atoms bonded to the Ga adatom is 0.51 Å away from the adatom. All other lateral or vertical displacements of the adlayer atoms are less than 0.1 Å.

Ga adatoms on (or in) the Ga adlayer were considered. These nlcc calculations indicate that a structure containing one additional Ga atom in each $3 \times 3$ cell is the best model for the observed $3 \times 3$ reconstruction. One may construct a class of such adatom-on-adlayer structures by adding threefold coordinated Ga atoms to the $1 \times 1$ adlayer. This addition lowers the symmetry from $1 \times 1$ to $n \times n$ where $1/(n \times n)$ is the fraction of added Ga atoms. We have determined that such structures with $n = \sqrt{3}$ and $n = 2$ are each unstable with respect to the $1 \times 1$ Ga adlayer. However, for $n = 3$ we find that the AOA structure becomes stable in Ga-rich conditions. In the $3 \times 3$ structure, the extra Ga atom resides only 0.9 Å above the adlayer plane, compared to a 1.35 Å separation in the $\sqrt{3} \times \sqrt{3}$ and 1.25 Å in the $2 \times 2$. In the absence of lateral relaxation, the Ga adatom must be positioned 1.8 Å above the adlayer to preserve a reasonable Ga-Ga distance. The larger inward relaxation of the adatom in the $3 \times 3$ structure is enabled by a 0.5 Å lateral relaxation of the nearest-neighbor Ga adlayer atoms, which allows the adatom to move much closer to the adlayer plane, thereby stabilizing the structure. We may therefore refer to the proposed structure as an in-plane adatom model, as illustrated in Fig. 4(b). Images of the calculated local density of states for this model are found to be in qualitative agreement with the experimental results.

We examined two types of $3 \times 3$ models in which two Ga atoms were added to the $1 \times 1$ adlayer: a trimer-in-vacancy model where an adlayer atom is replaced by a Ga trimer, and a structure having 2 Ga adatoms per $3 \times 3$ cell, with each placed in a threefold coordinated site. The total energies of these models were calculated with the nlcc approximation and were found to be less stable than the proposed $3 \times 3$ AOA structure by about 0.9 eV/($3 \times 3$) and 1.1 eV/($3 \times 3$) in the Ga-rich limit. From a comparison of energies of structures calculated with the nlcc and with the Ga-$3d$ electrons included

in the valence band, we think the maximum error in these relative energies is less than 0.5 eV/($3 \times 3$). [For example, in calculations for the $2 \times 2$ AOA model we found that the nlcc gave an energy relative to the $1 \times 1$ Ga-adlayer model which was within 0.04 eV/($2 \times 2$) of the full calculations.] It is clear that these nlcc calculations support the experimental determination that the $3 \times 3$ contains only one additional Ga atom per cell.

In conclusion, we have observed a new family of reconstructions on the GaN(000$\bar{1}$) surface. The $1 \times 1$ structure is determined to consist of a monolayer of Ga atoms bonded in atop sites above N atoms of a N-terminated bilayer. The $3 \times 3$ reconstruction consists of Ga adatoms bonded on top of this adlayer. Adatom-on-adlayer models for the other observed reconstructions are also possible, although such structures have not yet been explored in detail.

[1] S. Nakamura, T. Mukai, and M. Senoh, Appl. Phys. Lett. **64**, 1687 (1994); S. Nakamura *et al.,* Jpn. J. Appl. Phys. **35**, L74 (1996).

[2] M. Wassermeier, A. Yamada, H. Yang, O. Brandt, J. Behrend, and K. H. Ploog, Surf. Sci. **385**, 178 (1997).

[3] J. Neugebauer, M. Scheffler, J. E. Northrup, and C. G. Van de Walle (to be published); J. E. Northrup and J. Neugebauer, Phys. Rev. B **53**, 10477 (1996); J. E. Northrup, R. Di Felice, and J. Neugebauer, Phys. Rev. B **55**, 13878 (1997).

[4] M. E. Lin *et al.,* Appl. Phys. Lett. **62**, 702 (1993); W. C. Hughes *et al.,* J. Vac. Sci. Technol. B **13**, 1571 (1995); K. Iwata *et al.,* Jpn. J. Appl. Phys. **35**, L289 (1996); P. Hacke *et al.,* Appl. Phys. Lett. **69**, 2507 (1996); R. A. Held *et al.,* J. Electron. Mater. **26**, 272 (1997).

[5] F. A. Ponce, D. P. Bour, W. T. Young, M. Saunders, and J. W. Steeds, Appl. Phys. Lett. **69**, 337 (1996); B. Daudin, J. L. Rouvière, and M. Arlery, Appl. Phys. Lett. **69**, 2480 (1996).

[6] Using a growth condition identical with those reported in the present work, we have reproduced the RHEED results reported by Hughes *et al.* [4] for homoepitaxy on GaN layers grown by metalorganic vapor phase epitaxy. The surface polarity in this case is believed to be (0001). Apparently, the polarity is determined solely by the substrate and the initial nucleation layers in the growth.

[7] C. Hu, M. De Graef, A. R. Smith, R. M. Feenstra, and D. W. Greve (to be published).

[8] R. M. Feenstra, A. J. Slavin, G. A. Held, and M. A. Lutz, Phys. Rev. Lett. **66**, 3257 (1991).

[9] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).